Site Need Statement

General Reference Information

- 1 * Need Title: Separable Organic Phase Destruction, Removal, and Monitoring In Tank Waste
- ² * Need Code: RL-WT103
- Need Summary: The Hanford Site used organic solvent extraction processes for the recovery of plutonium, uranium and fission products. The separable organic material included normal paraffin hydrocarbon (NPH), tributyl phosphate (TBP), bis-di-2-ethyl hexyl phosphoric acid, and hexone. Although it was not a routine practice to discharge organic material to waste tanks, an uncertain amount of separable organic material was discharged to the tank farms at Hanford. As of December 2000, one single-shell tank (SST), C-103, is known to contain about 4,500 gallons of floating separable phase organic liquid comprised of TBP and NPH. Four other SSTs have been identified as containing lesser volumes of TBP and/or NPH entrained in the waste solids. In the past, there was evidence that some DSTs likely contained separable organic material, however, there is no current evidence of a separate organic phase in any of Hanford's twenty-eight DSTs.

The River Protection Project mission includes removal of the pumpable liquids from SSTs (interim stabilization) by FY 2004 and processing of tank waste at a Waste Treatment Plant (WTP) by FY 2007. Currently, a 25-ppm separable organic material limit has been imposed on WTP waste feed. It has been suggested that trace concentrations of separable organic material entrained in waste solids can be processed in the WTP with minimal impacts. The baseline plan for interim stabilization of C-103 has the floating separable organic layer and the aqueous liquid being pumped together to a designated DST. An alternative process for separately removing the organic layer prior to waste transfer from C-103 to the receiver DST has been evaluated and found to be viable but not cost effective.

Technology development can aid the handling of the C-103 organic layer and any other separable organic material that may be discovered during waste retrieval in support of WTP processing. Specifically, technology that could remove the C-103 organic layer down to the 25-ppm level, without entrainment of the radiologically-contaminated aqueous liquid could make that alternative cost effective. Currently available technology, such as floating weir skimmer pumps or continuous belt skimmers have been proposed but have not been shown to meet all criteria identified in the "Separable Organic Management Strategy" (Memo, CHG-0004873 R2, B. R. Estey (CHG) to J. J. Short (DOE-ORP), "Contract Number DE-AC27-99RL14047: Submittal of Separable Organic Management Strategy White Paper," dated November 17, 2000).

Technology development is also needed for an alternative that would capture the separable organic material in the solid phase and retain it there through retrieval and waste processing. A proposed technology for this capability includes absorbing the organic on solid carbon, which would be retained with the waste solids.

Technology development is also needed for an in-tank process to degrade the separable organic material. It has been observed that contact with high concentrations of hydroxide degrades TBP, the principal remaining separable organic material, to aqueous-soluble organic compounds. This process occurs very slowly if there is no mixing of the high hydroxide aqueous layer with the separable organic layer. Other in-tank methods for organic destruction should be proposed and evaluated.

A final technology development need involves detection of floating organic material in DSTs. The WTP feed limit of 25 ppm represents approximately 25-gallons in a 1,000,000-gallon waste tank. A 25-gallon layer of separable organic material across the waste surface is approximately 0.01 inch thick. Detection of this small volume in not currently achievable in Hanford waste tanks.

- 4 * Origination Date: FY 2001
- 5 * Need Type: Technology Opportunity
- 6 *Operation Office:* Office of River Protection
- 7 Geographic Site Name: Hanford Site
- 8 **Project:** Retrieval PBS No: RL-TW04

- National Priority:

 1. High Critical to the success of the EM program, and a solution is required to achieve the current planned cost and schedule.
 X 2. Medium Provides substantial benefit to EM program projects (e.g., moderate to high life-cycle cost savings or risk reduction, increased likelihood of compliance, increased assurance to avoid schedule delays).
 3. Low Provides opportunities for significant, but lower cost savings or risk reduction, may reduce the uncertainty in EM program project success.
- 10 Operations Office Priority:

Problem Description Information

Operations Office Program Description: The Single-Shell Tank (SST) Interim Closure Project is responsible for Program/Project Planning and Execution; Environment, Safety, Health, and Quality Assurance; Facility Operations; Engineering; Maintenance; Interim Stabilization; and Technology Development, Demonstrations, and Deployments necessary for the safe and cost effective storage, retrieval, immobilization, and closure of SST wastes, associated underground storage tanks, and ancillary piping and equipment. Safe storage of wastes includes day-to-day operations of the SST's and saltwell pumping operations to remove pumpable liquids from the SST's for transfer to double-shell tanks (DST's) to achieve interim stabilization and minimize the potential for SST leakage. Retrieval projects will be conducted to remove wastes from SST's for placement in DST's in support of waste feed delivery to the Waste Treatment Plant and eventual waste immobilization. An integral part of SST waste retrieval operations is leak detection, monitoring, and mitigation. Safe storage, retrieval, and closure activities associated with SST wastes are also supported by Special Projects and Vadose Zone Projects to characterize groundwater flow and contaminant transport phenomena, geohydrological conditions, and the nature and extent of contaminant plumes.

12 Need/Problem Description:

The WTP can accommodate trace quantities of separable organic material (<25ppm waste feed limit). No measurable effect is expected in the WTP Process or in glass product quality from trace quantities of separable organic material. In larger quantities, the separable organic material could cause degradation of the elastomer seals on retrieval pumps and the ethylene-propylene-diene-monomer (EPDM) type hoses. Separable organic material could also plug pretreatment filters requiring frequent back flushing and extra cleaning of the filters with special solutions and techniques. Separable organic material could coat the surfaces of ion exchange resins and reduce the cesium loading capacity. Finally, separable organic material could cause flammable gas concerns in the off-gas and vessel ventilation systems in the vitrification process for low-activity waste and high-level waste.

- ** | Program Baseline Summary (PBS) No.: TW04
- ** | Work Breakdown Structure (WBS) No.: 5.025.01.04302.04.01.01.01, 5.01.04.02.04.04
- ** TIP No.:

Functional Performance Requirements: The separable organic material destruction, separation, or detection technology needs to be able to address organic concentrations <25 ppm. The O&M Contractor has estimated that as much as 250 gallons of NPH could be evaporated in less than two months from a tank ventilated at a rate of 150 scfm at a temperature of 40 degrees centigrade. Using this value and assuming a mixing ratio of NPH:TBP of 2:1, it would take a few years to evaporate the NPH fraction of the organic in C-103.

A preliminary model was developed for predicting time requirements for alkaline hydrolysis of TBP at several different conditions. For the 4,500 gallons of separable organic material in C-103, it has been predicted that with an aqueous to organic ratio of 20, 0.5M hydroxide solution, and a temperature of 50 degrees centigrade, it would take 1.5 years to degrade 99.95% of the TBP. In a similar prediction at 40 degrees centigrade, it would take 4 years to degrade 99.95% of the TBP.

** **Schedule Requirements:** Interim stabilization of tank 241-C-103 must be completed by FY 2004 per Hanford Consent Decree.

14	Definition of Solution:
15 *	Targeted Focus Area: Tanks Focus Area (TFA)
16	Potential Benefits:
17 *	Potential Cost Savings: On the order of \$10 Million
18 *	Potential Cost Savings Narrative: Construction and installation of separable organic material removal and treatment options has a high capital cost. The cost of removing and treating the separable organic layer in C-103 alone has been estimated at \$8.8 to \$9.8 Million.
**	Technical Basis: As much as 2,490,000 liters (657,900 gallons) of separable organic material (TBP and NPH) was discharged to the Hanford tank farms over the operational period of the PUREX Plant. Much of the organic solvent has degraded, evaporated to the atmosphere, or was sent to condensate cribs. Current estimates suggest that from 34,000 liters (9,000 gallons) to 148,000 liters (39,000 gallons) of separable organic may still reside in tank wastes. This organic material may exist as a separate floating phase (continuous layer, pools, puddles, or sheen); emulsified droplets in the aqueous supernatant; and/or trapped or sorbed phases in the saltcake and sludge solids.
	There is evidence to suggest that most SSTs contain at least some organic material that is TBP or its degradation products. In many cases, the organic material appears to be trapped in the solid saltcake and sludge layers. Organic material released from solid phase layers during retrieval could remobilize to form a separate bulk phase that floats on the surface of the aqueous tank waste, if NPH is present. Analyses of gases within tank vapor spaces suggest that the SSTs contain a similar family of volatile organic compounds that would be expected as degradation products of TBP and NPH. Other direct and indirect evidence suggests that the occurrence of separable organic material may be a more global problem throughout the Tank Farm Complex at Hanford.
	The principle insoluble organic material suspected in the Tank Farms is a mixture of NPH and TBP. NPH is a straight-chained hydrocarbon with very low solubility in aqueous solutions. NPH forms immiscible phases in the presence of aqueous tank waste solutions.
	TBP and its degradation products are soluble, to varying degrees, in aqueous solutions and are typically found in many of Hanford's SSTs and DSTs. TBP is highly soluble in NPH. When associated with NPH, TBP does not dissociate into the aqueous phase and is armored against chemical hydrolysis. The mixture of TBP and NPH is less dense (0.876 gram/milliliter) than the aqueous tank waste. As a result, the mixture of TBP and NPH tends to float to the top of the aqueous wastes by gravity separation.
19	Cultural/Stakeholder Basis: Reviewers for DOE (Tank Advisory Panel – Chemical Reactions Subpanel), Washington State Department of Ecology, and other stakeholders have expressed concerns with saltwell pumping the organic and aqueous phases from SSTs to DSTs during interim stabilization operations.
20	Environment, Safety, and Health Basis: Safety is a moderate to strong discriminator for decisions regarding the handling of separable organic phases in tank wastes. All technological options will require an Unreviewed Safety Question (USQ) evaluation against the existing nuclear safety authorization basis (AB). Subsequent to a positive USQ determination, the AB would be changed to include the new technological option for implementation. The USQ determination activities associated with removal and treatment options will be extensive due to significant worker doses resulting from the handling of mixed organic and aqueous phases. Shielding and administrative controls will be required to assure conformance to the ALARA policy. Technological options for addressing the separable organic material will likely require special regulatory reviews and environmental permits.
21	Regulatory Drivers: Issues surrounding separable organic phases in SSTs must be resolved to avoid potential impacts to the Hanford Site Consent Decree for interim stabilization (saltwell pumping) of all SSTs by fiscal year 2004.
22 *	Milestones: TBD
23 *	Material Streams: Sludge, Salt, Liquid (RL-HLW-20)
24	TSD System: Single Shell Tank systems

25	<i>Major Contaminants:</i> Pu-238, 239, 240, 241; AM-241; U-238; C-14; Ni-59/63; Nb-94; Tc-99; I-129; Cm-242; Sr-90; Cs-137; Sn-126; Se-79; chromium; nitrate; nitrite; complexants (EDTA/HEDTA)	
26	Contaminated Media: Saltcake, Sludge, Supernatant. Tank waste consisting of high molarity sodium hydroxide/sodium nitrate solution containing saturated saltcake and/or sludge.	
27	<i>Volume/Size of Contaminated Media:</i> Estimated 39,000 gallons of separable organic in tank wastes. The single shell tanks are generally 75 ft. in diameter, and up to 40 feet deep with their tops buried about 10 feet below the ground surface.	
28 *	Earliest Date Required: September 2001	
29 *	Latest Date Required: September 2003 (to support FY 2004 completion of C-103 interim stabilization)	
Baseline Technology Information		
30	Baseline Technology/Process: There are several basic options to address the global concern of separable organic material in tank wastes. All options are challenged by the ability to detect a separable organic phase. Indirect methods for addressing the separable organic material include in-tank evaporation and alkaline hydrolysis. Several direct methods are available and represent various locations where separable organic material might be encountered and dispositioned. These include: (1) Remove and treat the separable organic material from each SST before retrieval, (2) Remove and treat the separable organic material during SST retrieval operations, (3) Remove and treat the separable organic material from each DST, (4) Consolidate the separable organic material in a single DST, (5) Remove the separable organic material during waste transfer to the WTP, and (6) Treat the separable organic material in the WTP. Technology Insertion Point(s): N/A	
31	Life-Cycle Cost Using Baseline:	
32	Uncertainty on Baseline Life-Cycle Cost:	
33	Completion Date Using Baseline: post 2020 for all SSTs/DSTs	
Points of Contact (POC)		
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^{*}Element of a Site Need Statement appearing in IPABS-IS
**Element of a Site Need Statement required by CHG